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A direct MO dynamics study on the photoreaction of permethylcyclopentasilane via a triplet energy surface $(Me_2Si)_5$ $(T_1) \rightarrow (Me_2Si)_4 + Me_2Si$:

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Abstract

Mechanism of photo-reaction of permethylcyclopentasilane $(Me_2Si)_5$ on the triplet excited state surface, $(Me_2Si)_5$ $(T_1) \rightarrow (Me_2Si)_4 + Me_2Si$:, has been investigated by means of direct molecular orbital (MO) dynamics method. Full dimensional potential energy surface calculated at the PM3 level was employed in the dynamics calculation: the total energy and energy gradient on each atom were calculated at each time step during the reaction. The vertical electronic transition from the ground (S_0) to the first excited triplet (T_1) states was assumed in the classical trajectory calculation. The calculations showed that the five-membered Si-ring is spontaneously changed to the four-membered ring without activation barrier on the T_1 surface. The photo-reaction of $(Me_2Si)_5$ is slightly faster than that of $(Me_2Si)_6$ due to the strong steric hindrance. Mechanism of the extrusion of silylene radical from the Si ring was discussed on the basis of theoretical results. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Direct MO dynamics; Polysilane; Photo-reaction; Permethylcyclopentasilane

1. Introduction

Photochemical property and the electronic structure of polysilane have been received much attention from experimental and theoretical points of view because they play an important role in photoresists, one-dimensional conductors, high-density optical data storage materials [1]. Cyclic-polysilane $(R_2Si)_n$ ($n = 4$–7 where R is alkyl group) is one of the photo-sensitive polysilanes to occur silylene extrusion at the excited state, and is also known as the intermediate to synthesize oligosilanes [1]. Studying of the reaction of the cyclosilanes at the excited state provides a detail information on the photochemistry of polysilane.

Permethyl-cyclopentasilane $(Me_2Si)_5$ is one of the cyclic polysilanes and its photo-reaction is expressed by

$$(Me_2Si)_5 + h\nu \rightarrow (Me_2Si)_4 + Me_2Si$$

Silylene radical is efficiently dissociated from $(Me_2Si)_5$ and a small-membered ring, i.e., cyclic-tetrasilane $(Me_2Si)_4$, is formed. The silylene radical is also generated from the photo-irradiation to the other numbered rings. In particular, the photo-irradiation of the cyclosilanes $(Me_2Si)_n$ ($n = 4$–7) gives smaller sized rings $(Me_2Si)_{n-1}$ and Me_2Si. It has been known that this reaction proceeds mainly via the singlet excited state (S_1) [2–4]. However, a recent experiment showed that the reaction proceeds on the triplet potential energy surface (T_1) as well as on the S_1 surface [5].

Drahnak et al. [2] reported that the silylene extrusion reaction of dodecamethyl cyclohexasilane $(Me_2Si)_6$ is occurred in 3-methylpentane and in methylcyclohexane matrices at 77 K [2].

$$(Me_2Si)_6 + h\nu \rightarrow (Me_2Si)_5 + Me_2Si:$$

The products (Me_2Si and $(Me_2Si)_5$) were characterized by UV-Vis and infrared spectroscopies. The similar reaction was observed in argon matrix at 77 K. The reaction was also observed in argon matrix at 10 K [3].

In a previous paper, we investigated the photo-reaction of $(Me_2Si)_6$ by means of direct MO dynamics method [6]. The calculations show that the reaction is spontaneously occurred on the T_1 state and is completed within 1.0 ps which is much faster in spite of the heavy atom (silylene radical Me_2Si) extrusion processes. This is due to the fact that bonding nature of Si–Si bond is strongly changed at the excited state.

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In the present study, we extend the direct MO dynamics calculation to the similar photo-chemical reaction of $(Me_2Si)_5$

$$(Me_2Si)_5 + h\nu \rightarrow (Me_2Si)_5(T_1) \rightarrow (Me_2Si)_4 + Me_2Si:$$

reaction 1

in order to obtain more general feature in the cyclic polysilane. For this reaction system, Ishikawa and Kumada [4] reported that the photochemical degradation reaction of $(Me_2Si)_5$ as well as in $(Me_2Si)_6$ was observed in cyclohexane solution at 318 K [4]. Therefore, studying reaction 1 would provide more detailed information of photo-chemistry of cyclic-polysilanes.

2. Method of calculations

In general, the classical trajectory is performed on an analytically fitted potential energy surface as previously carried out by us [7–11]. However, it is not appropriate to predetermine the reaction surface of reaction 1 due to the large number of degrees of freedom ($3N-6 = 129$ where N is number of atoms in the reaction system). Therefore, in the present study, we applied the direct trajectory calculation with all degrees of freedom [12–16]. The energy gradients on all atoms were calculated at the PM3-MO level at each time step.

In the trajectory calculation, we used optimized geometry of $(Me_2Si)_6$ as an initial structure. At a starting point of the trajectory calculation, atomic velocities for all atoms were adjusted to give a temperature of 300 K. The potential energy (total energy) and energy gradients at each time step was calculated at the PM3-MO level [17–19][1]. The program code to calculate the trajectory was made by our group [12–16][2].

In the calculation of the classical trajectory, we assumed that each atom moves as a classical particle on the PM3 multi-dimensional potential energy surfaces. The equations of motion for n atoms in a molecule are given by

$$m_i \frac{dv_{\mu i}}{dt} = F_{\mu i}$$

$$\frac{dx_{\mu i}}{dt} = v_{\mu i}$$

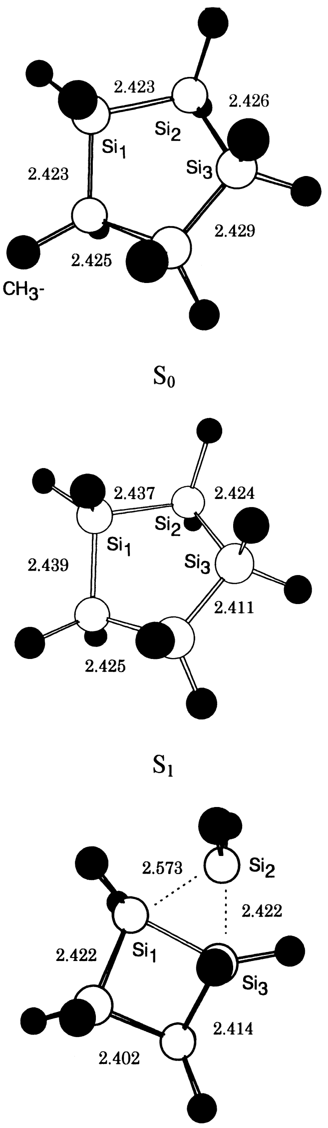
where $x_{\mu i}$ ($\mu = 1,2,3$) are the three Cartesian coordinates of the ith atom with mass m_i, $F_{\mu i}$'s are the three components of the force acting on the ith atom. These equations were numerically solved by the Runge–Kutta method. No symmetry restriction was applied in the calculation of the gradients in the Runge–Kutta method. The time step size was chosen by 0.2 fs.

3. Results

3.1. Structures of $(Me_2Si)_5$ at the ground and excited states

Firstly, the structure of $(Me_2Si)_5$ at the ground state (S_0 state) was fully optimized by PM3 method. The optimized structure is illustrated in Fig. 1 (S_0). The averaged distance of Si–Si bonds was calculated to be 2.4252 Å which is as long as that of $(Me_2Si)_6$ (2.4285 Å) [6]. Angle of Si–Si–Si was calculated to be 104.85° which is comparable to that of $(Me_2Si)_6$ (105.8°).

Next, the structure for the triplet state (T_1) was optimized under no-symmetry restriction (i.e. C_1 symmetry). The geometry optimization at the T_1 state gave a large distorted structure from that at the ground state (S_0): the interatomic distance between Si_1 and Si_3 atoms was calculated to be



S_0

S_1

T_1

Fig. 1. Optimized structures of $(Me_2Si)_5$ at the ground state (S_0), the singlet excited state (S_1), and the triplet state (T_1) calculated by PM3-CI method.

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[1] Program for the dynamics calculation was made by our group.

[2] Program for the dynamics calculation was made by our group.

2.5579 Å which is significantly shorter than that of S_0 state (3.7240 Å). The bond distance between Si_1–Si_2 was 2.5730 Å which is slightly elongated, whereas the distance for the other Si–Si bonds was ca. 2.42 Å, which is close to a normal Si–Si distance. These results strongly indicated that a silylene radical Me_2Si: can be dissociated from the silane ring $(Me_2Si)_5$ on the T_1 potential energy surface.

For comparison, the structure of $(Me_2Si)_5$ for the singlet excited state (S_1) was also optimized under no-symmetry restriction by means of PM3-CI method. The optimized structure is illustrated in Fig. 1 (S_1). At the S_1 state, the structure of the Si skeleton was hardly changed from that at the ground state (S_0). This means that a local minimum exists for the silylene extrusion reaction on the first excited singlet state (S_1).

3.2. Dynamics of the silylene extrusion reaction

As shown in previous section, it is expected that the structure of $(Me_2Si)_5$ is drastically changed by the electronic excitation to the T_1 state. This suggests that $(Me_2Si)_5$ is a photo-sensitive molecule as well as $(Me_2Si)_n$ ($n = 6$ and 7). In order to elucidate the dynamics on the excited state, the direct MO dynamics calculations is carried out for $(Me_2Si)_5$ on the T_1 surface. The optimized structure for the ground state $(Me_2Si)_5$ was used as an initial structure in the dynamics calculation.

The result of the dynamics calculation is given in Fig. 2. Potential energy curve calculated as a function of reaction time (Fig. 2(A)) shows that the energy of system is suddenly lowered at very short time region (0.0–0.20 ps, the first stage of reaction I) and gradually lowered at longer time region (0.40–1.20 ps). At time 1.40 ps, the reaction was terminated. An intermediate complex expressed by $(Me_2Si)_4$...Me_2Si was formed due to no-excess energy at time zero.

Time dependence of the atomic distances is plotted in Fig. 2(B). At the time zero, the interatomic distance of Si_1–Si_3 was 3.7240 Å. This distance was largely varied at the first stage (0.0–0.20 ps). After 0.22 ps, the distance was 2.50 Å which is much shorter than that of the initial state and is close to a normal Si–Si distance. This implies that the single bond between Si_1 and Si_3 is newly formed by proceeding the reaction at the triplet energy surface. Above feature is also seen in time-dependence of bond angle (Si_1–Si_2–Si_3): the angle was changed from 100° to 60° by the excitation (Fig. 2(C)). These results indicate that the silylene radical (including the silicon atom of Si_2) is extruded from the five-membered ring, and then the four-membered ring is newly yielded. Time scale of this reaction on the T_1 surface was 0.2–0.4 ps which is much fast in spite of heavy atoms (silylene radical) extrusion reaction.

3.3. Time dependence of the bond population

In order to analyze the bond scission and formation processes during the reaction, we monitored a simple Mulliken population between all the Si atoms. The results are given in Table 1. At the ground state (S_0), all Si–Si bonds have a normal bond population calculated by 0.354. In contrast, at the T_1 state the population for one of the Si–Si bonds, Si_1–Si_2, has a negative sign (−0.983), suggesting that the bond becomes strongly repulsive at the T_1 state. This may cause a bond scission between Si_1 and Si_2 atoms. It should be noted here that population of Si_1–Si_3 was positive (0.037) in spite of the long interatomic distance (3.7240 Å). The populations for Si_1, Si_2, and Si_3 atoms were widely changed as a function of reaction time. At the final stage ($t = 1.50$ ps), the populations for Si_1–Si_2 and Si_1–Si_3 bonds were calculated to be −0.422 and −0.327, respectively, suggesting that the silylene radical including Si_2 atom is strongly repulsive to both Si_1 and Si_3 atoms. On the other hand, the population between Si_1 and Si_3 atoms was 0.384 which is large enough to form a Si–Si single bond. These results strongly indicate that the five-membered ring is spontaneously changed to the four-membered ring and silylene radical on the triplet energy surface.

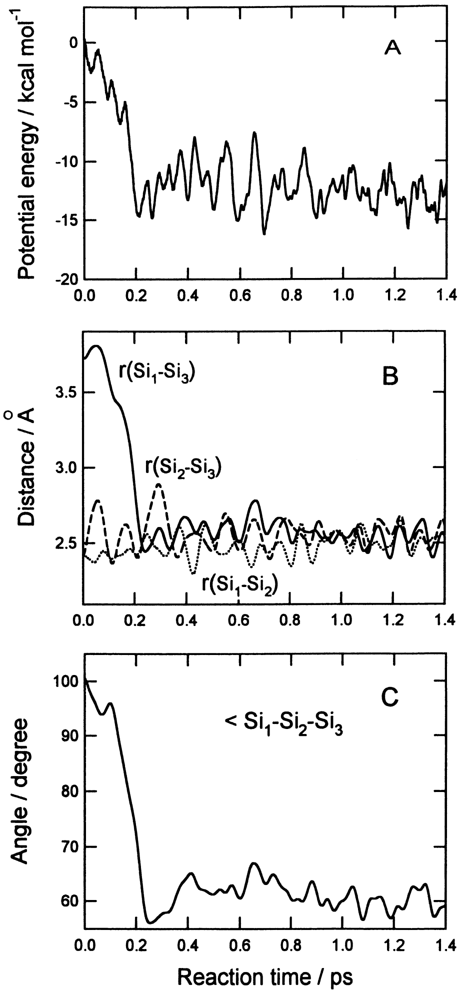

Fig. 2. Sample trajectory calculated by the direct PM3-MO dynamics method with T_1 potential energy surface. (A) potential energy, (B) interatomic distances, and (C) angle of Si_1–Si_2–Si_3 versus reaction time.

Table 1
Bond populations calculated as a function of reaction time

State	Time (ps)	Bond population			
		Si_1–Si_3	Si_1–Si_2	Si_2–Si_3	Si_4–Si_5
S_0	0.0	−0.06	0.354	0.354	0.357
T_1	0.0	0.037	−0.983	0.236	0.358
	0.10	0.043	0.226	−1.046	0.357
	0.15	−0.005	0.276	−0.635	0.356
	0.20	−0.183	0.280	−0.681	0.326
	0.40	−0.073	0.243	−0.501	0.352
	0.80	0.206	−0.163	−0.423	0.324
	1.50	0.384	−0.422	−0.327	0.333

Dissociating silylene is composed of Si_2 atom.

3.4. Spin orbitals

Spin orbitals as a function of reaction time are illustrated in Fig. 3. At time zero, an unpaired electron was localized on one of the Si–Si bonds. At time = 0.1 ps, the unpaired electron was concentrated slightly on the silylene moiety (Me_2Si) in consequence of the extension of Si–Si bond. At time 0.22 ps, almost spin density was localized on π-orbitals of silylene radical as shown in Fig. 3. Thus spin orbital clearly shows that the extrusion of silylene radical from the five membered ring occurs as reaction time increases.

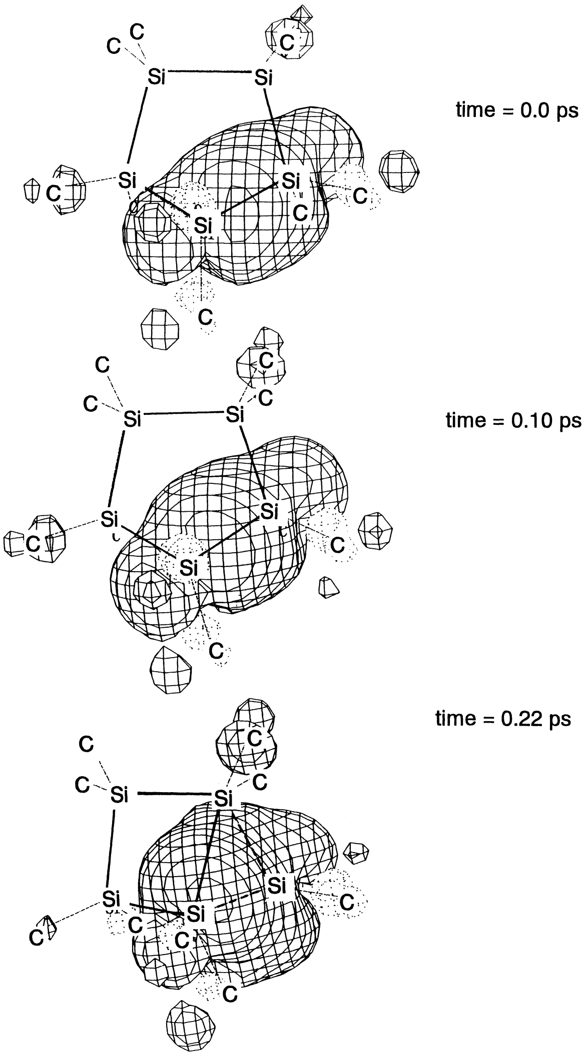

Fig. 3. Snapshots of the geometry and contour maps of spin density on $(Me_2Si)_5$ as a function reaction time on the T_1 potential energy surface. Bold line indicates the Si–Si skeleton.

4. Discussion

Almost all the previous studies have mainly considered singlet energy surface (S_1) for reaction 1 [2–4]. In a few studies, the reaction from the triplet state was observed experimentally [5]. As a theoretical point of view, Ramsey pointed out that both $^1(\sigma - \sigma^*)$ and $^3(\sigma - \sigma^*)$ excited states correlate to the silylene radical dissociation channel [20]. Therefore, it is important to elucidate the dynamics via the triplet surface for deeper understanding in the photoreaction of cyclic-polysilanes. From this point of view, the dynamics of the silylene extrusion reaction on the triplet state (T_1) surface have been investigated in this study. The dynamics calculation strongly indicated that the photochemical extrusion reaction of Me_2Si: proceeds on the T_1 surface as well as the S_1 surface.

Photoreaction mechanism of $(Me_2Si)_5$ is qualitatively discussed in terms of the orbital interactions. Schematic representation of the orbital interaction on the Si_1–Si_2–Si_3 moiety during the photoreaction process is illustrated in Fig. 4. At the ground state (S_0), the highest occupied molecular orbital (HOMO) shows that all Si–Si bonds have a bonding nature, suggesting that the regular cyclic structure is most stable. At the T_1 state, the orbital interaction of Si–Si bonds changes to anti-bonding type and the unpaired electrons are delocalized on three membered Si–Si–Si skeleton.

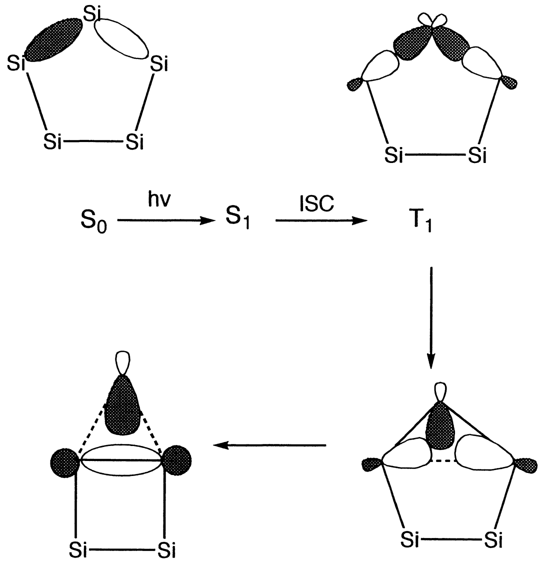

Fig. 4. Schematic representation of orbital interactions of the Si atoms at the T_1 excited state along the reaction coordinate. ISC means intersystem crossing between S_1 and T_1 states.

The interaction between Si_2 and Si_j (j=1 and 3) is composed of strong anti-bonding interaction. The silylene extrusion will have occurred on this site. Magnitude of the anti-bonding interaction may be enough for the elongation of Si_2–Si_j bonds to occur. Accompanying with the slight elongation of Si_2–Si_j bonds, the Si_1–Si_3 bond is newly formed because of the same orbital phases. After more elongation of the Si_2–Si_j bonds, the Si_1–Si_3 bond is completely formed and silylene radical is dissociated from the four membered ring. This mechanism is in reasonable agreement with our previous model proposed for the photoreaction mechanism in $(Me_2Si)_6 \rightarrow (Me_2Si)_5 + Me_2Si(T_1)$ [6] the silylene radical is extruded from the six-membered ring $(Me_2Si)_6$ at the T_1 state. The reaction in both cases (i.e. $n = 5$ and 6) is explained reasonably in terms of the same mechanism. Hence, the present mechanism would be general in photoreaction of the cyclic Si compounds.

Several approximations to calculate the potential energy surface and to treat the reaction dynamics were introduced in this study. Firstly, we assumed that $(Me_2Si)_5$ (T_1) has no excess energy at the initial point of the trajectory calculation (time = 0.0 ps). This may cause a change of lifetime for $(Me_2Si)_4\cdots Me_2Si$ intermediate where the silylene radical interacts weakly with $(Me_2Si)_4$. Hence, the present calculation showed that the trajectory is trapped in the intermediate region, while the silylene radical was not completely not escaped from $(Me_2Si)_4$. The dissociation of Me_2Si may occur in the case of higher excess energy and in matrices. These effects were not considered in the present calculations. It should be noted therefore that the present model is limited in the case of no excess energy. Secondly, we assumed PM3 multi-dimensional potential energy surface in the trajectory calculations throughout. More accurate wave function may provide deeper insight in the dynamics. Despite several assumptions are introduced here, the results enable us to obtain valuable information on the photoreaction process in $(Me_2Si)_6$.

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